The evolution of vacancy-type defects in silicon-on-insulator structures studied by positron annihilation spectroscopy

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Variable-energy positron annihilation spectroscopy (VEPAS) has been applied to the study of the formation and evolution of vacancy-type defect structures in silicon (Si) and the 1.5 μm thick Si top layer of silicon-on-insulator (SOI) samples. The samples were implanted with 2 MeV Si ions at fluences between 10^{13} and 10^{15} cm^{-2}, and probed in the as-implanted state and after annealing for 30 min at temperatures between 350 and 800 °C. In the case of SOI the ions were implanted such that their profile was predominantly in the insulating buried oxide layer, and thus their ability to combine with vacancies in the top Si layer, and that of other interstitials beyond the buried oxide, was effectively negated. No measurable differences in the positron response to the evolution of small clusters of n vacancies (V_n, $n \sim 3$) in the top Si layer of the Si and SOI samples were observed after annealing up to 500 °C; at higher temperatures, however, this response persisted in the SOI samples as that in Si decreased toward zero. At 700 and 800 °C the damage in Si was below detectable levels, but the VEPAS response in the top Si layer in the SOI was consistent with the development of nanovoids. © *2011 American Institute of Physics*. [doi:10.1063/1.3605487]

While the evolution of vacancy-type defects in silicon is of fundamental interest,[1] its control has long played an important role in the development of useful device structures,[2] for example, in gettering metallic impurities,[3] wafer separation,[4] and the suppression of dopant diffusion.[5–7]

Kalyanaraman *et al*.[8,9] used Au labeling to study the formation of nanovoids in Si. The aim of the current research is to investigate the evolution of vacancy-type defects in Si with annealing temperature, from divacancies in as-implanted samples through small clusters of n vacancies V_n ($n = 3$–6) to nanovoids, using the technique of variable-energy positron annihilation spectroscopy (VEPAS). Of particular interest is the comparison of this vacancy evolution in the equivalent topmost Si layers in Si and silicon-on-insulator (SOI) samples.

In order to optimize the creation of excess vacancies in a near-surface Si layer by Si ion implantation an SOI structure is employed, so that the Si ions which create the vacancies are implanted into the buried oxide (BOX) layer comprising SiO_2. This process creates an excess vacancy concentration in the top Si layer by isolating excess interstitials either within or beyond the BOX layer.[8–10]

In VEPAS[11] controllable-energy positrons are implanted into the sample under study, thermalize and diffuse before annihilation with electrons with the emission of two gamma photons of energies close to 511 keV ($m_e c^2$). The extent of the Doppler broadening of the annihilation line at about 511 keV, usually characterized by the line shape parameter, S, is a measure of the average electron momentum characteristic of an annihilation site. The average momentum of electrons annihilated by positrons trapped in vacancies is lower than in bulk Si, and thus the Doppler broadening of the annihilation radiation is less, the annihilation line is narrower, and the parameter, S, is higher than for bulk Si. In contrast, the annihilation of positrons trapped in vacancies in SiO_2 is characterized by an S which is lower than in the bulk,[12] a result of the enhanced sensitivity of trapped positrons to oxygen electrons. Finally, VEPAS gives some measure of depth selectivity via control of the incident positron energy, E.

Czochralski (Cz) Si and SOI samples were implanted at room temperature with 2 MeV Si ions at fluences of 10^{13}, 5×10^{13}, 10^{14}, and 5×10^{14} cm^{-2} at the University of Surrey Ion Beam Centre. In the SOI samples, the thickness of the top Si layer is 1.5 μm, and the BOX layer is 1 μm thick. Stopping and Range of Ions in Matter (SRIM) simulations[13] indicate that over 90% of the Si ions are implanted into the SiO_2 layer, with a projected range of 1.76 μm.

The samples were measured using the University of Bath positron beam system,[14] in the as-implanted state and after annealing for 30 min at temperatures from 350 to 800 °C. The choice of these annealing temperatures was informed by an earlier study of the evolution of vacancy-type damage in implanted Si,[15] which suggested that at 350 °C divacancies existing in as-implanted Si may form small clusters,[16] at 470 °C they form the stable hexavacancy,[17] and at 700 °C they are completely annealed away.

Illustrative examples of the raw data are shown in Figs. 1 and 2 for the highest of the four ion fluences used; data for the lower fluences showed no features implying different behavior.

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All data sets were fit using the standard code VEPFIT,[18] which fits values of S and the effective positron diffusion length, L, for chosen layers; in this case 0–1500 and 1500–2500 nm. Fits, represented by the solid lines in Figs. 1 and 2, were only accepted if they yielded self-consistent values of S and L for each layer, using the calculations of Hakala *et al.*[19] as a guide for the characteristic S values of V_n, with $n = 2$ to 6.

The broad dips in $S(E)$ at $E \sim 20$ keV are the result of annihilation in the BOX layer; the S parameter for SiO_2 is lowered by ion implantation damage (and increases after annealing as the damage is removed). For clarity, we shall consider the defect evolution in the samples implanted with the highest ion fluence, 5×10^{14} cm^{-2}, since the data for this sample illustrate all of the major results of this study.

The VEPAS response in the top Si layer in the SOI and Si samples was essentially indistinguishable in the as-implanted state and after annealing at 350 and 470 °C. Fits for the as-implanted samples suggest the formation of divacancies in the Si layer with an average concentration $C_D \sim 2.5 \times 10^{19}$ cm^{-3} and, after annealing at 350 °C, small vacancy clusters (average size V_3) at $\sim 10^{19}$ cm^{-3}, as expected. C_D (for one type of defect) is calculated from fitted S or L values; for example, for divacancies,

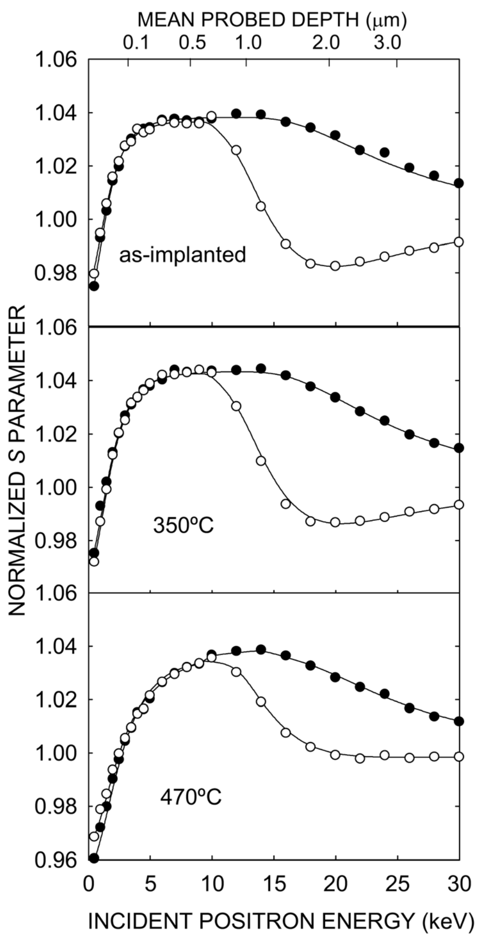

FIG. 1. S parameter vs incident positron energy for Si (filled circles) and SOI (open circles) implanted with 2 MeV Si ions at a fluence of 5×10^{14} cm^{-2}, and after annealing for 30 min at 350 and 470 °C. Solid lines are fits to the data using VEPFIT. Mean probed depths are computed from $z = 17.2\ E^{1.6}$ nm, with E in keV.

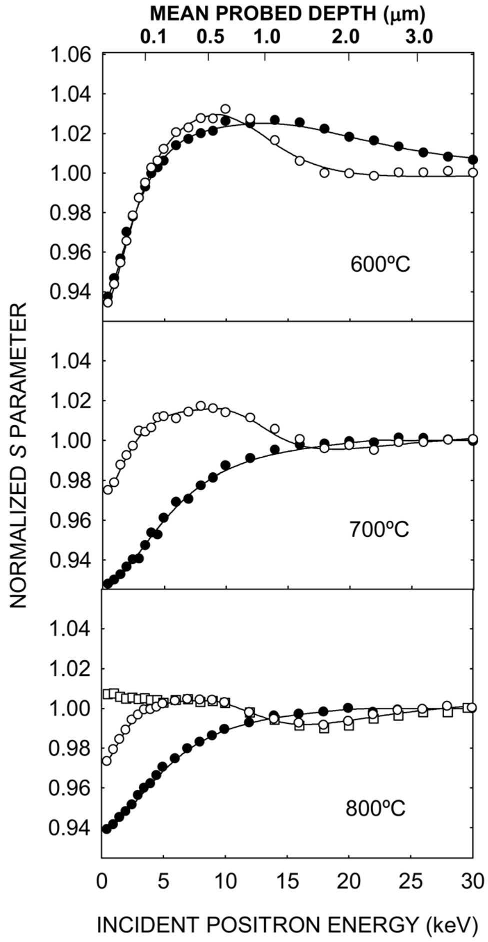

FIG. 2. S parameter vs incident positron energy for Si (filled circles) and SOI (open circles) implanted with 2 MeV Si ions at a fluence of 5×10^{14} cm^{-2}, after annealing for 30 min at 600, 700, and 800 °C. Solid lines are fits to the data using VEPFIT. The plots for the 800 °C annealed samples also include data for SOI after HF etching of the surface oxide (open squares). Mean probed depths are computed as in Fig. 1.

$$C_D = 6.7 \times 10^{17}(S - 1)/(S_D - S)\mathrm{cm}^{-3}, \qquad (1)$$

where S_D is the S value characteristic of the defect.[19]

After annealing at 470 °C, however, best fits of the SOI and Si data are obtained with $\sim 3 \times 10^{18}$ cm^{-3} trivacancies in the top Si layer (0–1500 nm) and hexavacancies only in Si near to the damage peak at a concentration of $\sim 2.5 \times 10^{17}$ cm^{-3}. These absolute values are thought to be correct to within 50%, most of the uncertainty coming from the value taken for the specific trapping rate, here taken as $3.4\ n^{1/2} \times 10^{14}$ s^{-1} for V_n.[20] The small vacancy clusters appear to survive in the top layer of the SOI after annealing at 600 °C, whereas 65% are annealed away in the Si sample.

The most dramatic change was seen after annealing at 700 °C. In all Si samples there is effective annealing of all vacancy-type damage to levels below the VEPAS sensitivity limit. However, in the top Si layer in the SOI samples there is evidence of some residual vacancy response in the low-fluence samples, and is most evident in the raw data for the highest-fluence sample (Fig. 2). The vacancy damage has evolved so that the average S value in the layer is 1,015, $L =$ 50 nm. This combination of S and L (in which both have small values) is not consistent with trapping by defects of any size up to the maximum identifiable by VEPAS ($\sim V_{20}$). One cannot invoke near-surface or interface electric fields to explain the data, as the same short L is not seen in the lower-fluence SOI nor in any of the Si samples. The only remaining possibility is that a high fraction of the small vacancy clusters in the top Si layer have agglomerated to form voids or small cavities. In a VEPAS and TEM study of voids in Si created by He implantation and annealing, Simpson *et al.*[21] reported that the measured S for positrons trapped in voids is approximately unity, i.e., close to that for undefected Si. The S-parameter for V_n increases with n until saturation occurs at $n \sim 20$ (Ref. 22) but, as the cluster size grows further, the positron is no longer quantum mechanically localized but instead sees the void boundary as a clean, internal Si surface, whose characteristic S parameter is only slightly higher than that for bulk Si.

This model of void formation is supported further by the data after annealing at 800 °C. At this stage the data are consistent with 100% void formation (i.e., $S \sim 1$) with $L = 40$ nm. In order to check that the data were not obscuring a real ($S > 1$) vacancy response, the native surface oxide was etched away with hydrofluoric acid; in the resultant data (also in Fig. 2) the same $S \sim 1$ response is seen in the top Si layer.

In order to estimate the average size of the voids formed after annealing at 800 °C, the trapping was treated using the diffusion limited trapping model, which is applied when the defects are large and widely separated. The positron trapping rate is then governed by the probability that a diffusing positron will *encounter* a defect site; once this occurs, then the positron is trapped.[23] The positron trapping rate, κ, is given by,

$$\kappa = 4\pi D_+ RN, \tag{2}$$

where D_+ is the positron diffusion constant [$= 2.7$ cm^2 s^{-1} in perfect Si (Ref. 24)], R is the radius of the trapping site, and N is the defect concentration. κ is first obtained from knowledge of L in the Si layer (40 nm) and the maximum possible value of L ($= L_+ = 250$ nm) in undefected Si:

$$\kappa = \lambda\left[(L_+/L)^2 - 1\right], \tag{3}$$

where λ is the positron decay rate in undefected Si [$= 4.54 \times 10^9$ s^{-1} (Ref. 24)]. This gives $\kappa = 1.7 \times 10^{11}$ s^{-1} from Eq. (3) and thus, using Eq. (2), $RN \approx 5 \times 10^9$ cm^{-2}.

We now assume that all 3×10^{18} cm^{-3} V_3 clusters observed after annealing the sample at 600 °C agglomerate to form voids. The number of vacancies per void, n, is therefore

$$n = 9 \times 10^{18}/N = 180R \ (R \text{ in nm}). \tag{4}$$

Now, if one assumes that each vacancy occupies a volume, v_1, equal to that occupied by an atom of Si, $v_1 = 0.02$ nm^3, then a void of radius R containing n vacancies has a volume of $4\pi R^3/3 = nv_1 = (180R)(0.02)$ nm^3 which, when solving for R, gives $R \approx 0.93$ nm. This model thus implies the existence of voids of $\sim$1.8 nm diameter containing, on average, 170 vacancies at a concentration of $\sim 5 \times 10^{16}$ cm^{-3}.

In summary, the evolution of vacancy-type defects in self-implanted Si follows the expected behavior. However, in the top Si layer of SOI, at 600 °C there are signs that vacancy damage is surviving more readily than in bulk Si, and at 700 and 800 °C a considerable VEPAS response remains, consistent with the formation of nanovoids of diameter $\sim$1.8 nm. It is presumed that this is a result of the increased probability for vacancy clusters to agglomerate rather than be annihilated by recombination with interstitials or by other methods in the top Si layers of the SOI samples, in agreement with the conclusions of Kalyanaraman *et al.*[9,10]

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